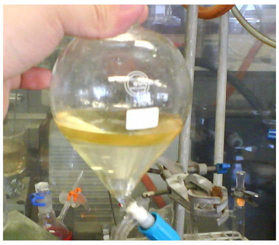
Sample Solutions Exercise 13

Exercise 13.1: Stability of thermodynamical systems (7P)



Consider a system which exchanges energy and volume with an external reservoir.

(a) Show that the difference of the heat capacities is given by

$$C_p - C_V = T\left(\frac{\partial H}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

Hint: Compare the differentials for $H(T,V)$ and $H(T,p)$ and try to express $\mathrm{d}V$ in terms $\mathrm{d}P$ and $\mathrm{d}T$. Finally substitute the heat capacities $C_{p,V} = T\left(\frac{\partial H}{\partial T}\right)_{p,V}$. (2P)

(b) Verify that $C_p - C_V = \frac{VT\alpha^2}{\kappa_T}$, where $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ is the thermal expansion coefficient and $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ is the isothermal compressibility. (2P)

(c) Prove that heat capacities and compressibilities have the same ratio, i.e. $\frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_H}$. (1P)

(d) Use (b), (c) and the properties of κ_T discussed in the lecture to show that the condition of global stability requires the inequalities (1P)

$$C_P \geq C_V \geq 0 \quad \text{and} \quad \kappa_T \geq \kappa_H \geq 0\,.$$

(e) Explain these inequalities on intuitive grounds. (1P)

Sample Solution

(a) The entropy expressed as a function of T, V has the differential

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial H}{\partial V}\right)_T \mathrm{d}V\,.$$

Similarly, the entropy expressed as a function of T, p possesses the differential

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p\,.$$

To compare both forms we consider the volume V as a function of temperature and pressure $V(T,p)$. Then

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p$$

Inserting this into the first equation yields

$$\mathrm{d}H = \left[\left(\frac{\partial H}{\partial T}\right)_V + \left(\frac{\partial H}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p\right] \mathrm{d}T + \left(\frac{\partial H}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p$$

Comparing this equation with the second one we arrive at:

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_V + \left(\frac{\partial H}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \qquad (*)$$

and

$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial H}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T$$

The last equation is simply the chain rule, while the first one is non-trivial. Inserting the heat capacities it reads

$$C_p - C_V = T \left(\frac{\partial H}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

(b) In the first term on the r.h.s. we use the Maxwell relation

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V .$$

With the coefficient

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

we thus obtain the intermediate result

$$C_p - C_V = T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = TV\alpha \left(\frac{\partial p}{\partial T}\right)_V .$$

The remaining partial derivative has to be transformed as follows. Given an equation of state $V(p,T)$ we start with the differential

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p .$$

Now let us assume that the volume is constant, hence $\mathrm{d}V = 0$. Therefore, we divide the equation

$$0 = \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p$$

by $\mathrm{d}T$, giving

$$0 = \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V .$$

Hence

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} .$$

With the isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

this relation can be written as

$$\left(\frac{\partial p}{\partial T}\right)_V = +\frac{\alpha V}{V\kappa_T}\,.$$

Inserting this back into the 'intermediate' result, we arrive at

$$C_p - C_V = TV\alpha\frac{\alpha V}{V\kappa_T} = \frac{TV\alpha^2}{\kappa_T}\,.$$

(c) For the ratio

$$\frac{C_p}{C_V} = \frac{\left(\frac{\partial H}{\partial T}\right)_p}{\left(\frac{\partial H}{\partial T}\right)_V}$$

we would like to reexpress the nominator in the same way as in (b). To this end we consider the equation of entropy relation $p(H,T)$ at constant pressure so that

$$0 = \mathrm{d}p = \left(\frac{\partial p}{\partial H}\right)_T \mathrm{d}H + \left(\frac{\partial p}{\partial T}\right)_H \mathrm{d}T\,.$$

Dividing by $\mathrm{d}T$ and assuming that $\mathrm{d}H/\mathrm{d}T$ at constant pressure is just $\left(\frac{\partial H}{\partial T}\right)_p$, we get

$$0 = \left(\frac{\partial p}{\partial H}\right)_T\left(\frac{\partial H}{\partial T}\right)_p + \left(\frac{\partial p}{\partial T}\right)_H\,,$$

i.e.

$$\left(\frac{\partial H}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_H}{\left(\frac{\partial p}{\partial H}\right)_T}\,.$$

Similarly one can show that

$$\left(\frac{\partial H}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_H}{\left(\frac{\partial V}{\partial H}\right)_T}\,.$$

Hence

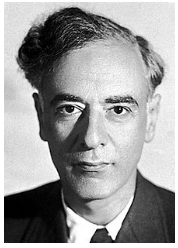
$$\frac{C_p}{C_V} = \frac{\left(\frac{\partial p}{\partial T}\right)_H\left(\frac{\partial V}{\partial H}\right)_T}{\left(\frac{\partial p}{\partial H}\right)_T\left(\frac{\partial V}{\partial T}\right)_H} = \frac{\left(\frac{\partial V}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial p}\right)_H} = \frac{\kappa_T}{\kappa_H}\,.$$

(d) The stability criterion (see lecture notes) requires the volumetric heat capacity to be positive ($C_V \geq 0$). The same applies to the thermal expansion coefficient α and the isothermal compressibility κ_T. Therefore, in part (b) we have proven that in a stable system $C_p \geq C_V \geq 0$.
Part (c) shows that the ratio of κ_T and κ_H is the same as that of the heat capacities. Thus, knowing that κ_T is positive, we can conclude that $\kappa_T \geq \kappa_H \geq 0$.

(e) If the system has a negative heat capacity, then it releases energy when heated, therefore it begins to heat itself. This happens e.g. in an explosive. Likewise, if the compressibility of a material is negative, it responds to a compression with a decrease of the counterpressure, leading to a sudden collapse. The relation $C_p \geq C_V$ is reasonable since a gas at constant pressure expands when heated, hence it performs work. This will require more energy to reach a certain temperature increase than in a system at constant volume. The relation $\kappa_T \geq \kappa_H$ is not easily interpretable.

Exercise 13.2: Landau theory **(5P)**

Consider a thermodynamical system with the free energy



$$F(\phi, T) = \frac{1}{2}\gamma(T^2 - T_0^2)\phi^2 - \frac{1}{3}\alpha T\phi^3 + \frac{1}{4}\lambda\phi^4\,,$$

where α, γ, λ, and T_0 are positive parameters.

(a) Determine the extrema of F as a function of ϕ for given T. (1P)

(b) Show that for $T < T_0$ there is no discontinuous phase transition. (1P)

(c) Prove that for $T > T_0$ the system exhibits a discontinuous phase transition. Compute the corresponding transition temperature $T_c(\alpha, \gamma, \lambda)$. (2P)

(d) Calculate the jump $\Delta\phi$ of the order parameter at $T = T_c$. (1P)

Sample Solution

(a) Solving $\frac{\partial F}{\partial \phi} = \gamma(T^2 - T_0^2)\phi - T\alpha\phi^2 + \lambda\phi^3 = 0$ we get the solutions

$$\phi_0 = 0\,, \quad \phi_\pm = \frac{T\alpha \pm \sqrt{T^2\alpha^2 - 4T^2\gamma\lambda + 4T_0^2\gamma\lambda}}{2\lambda}$$

(b) First we classify the extremum at $\phi_0 = 0$ by computing

$$F''(\phi_0) = F''(0) = \gamma(T^2 - T_0^2).$$

For $T < T_0$ this is negative, hence at $\phi_0 = 0$ we have a local maximum and therewith this solution is unstable. Consequently, we expect the curve to exhibit two local minima at $\phi_- < 0$ and $\phi_+ > 0$ (in fact, the argument of the square root is positive and larger than $T^2\alpha^2$). To find out which is the deeper minimum we compute the difference

$$F(\phi_+) - F(\phi_-) = -\frac{T\alpha\Big(4T_0^2\gamma\lambda + T^2(\alpha^2 - 4\gamma\lambda)\Big)^{3/2}}{12\lambda^3} < 0.$$

Hence we can conclude that ϕ_+ is the stable solution in this case.

(c) For $T > T_0$ we know that $\phi_0 = 0$ is a local minimum. In this region of the phase diagram we have to distinguish two cases:

- $\alpha^2 > 4\gamma\lambda$: Here the square root is real and the two solutions $\phi_\pm$ are real.
- $\alpha^2 < 4\gamma\lambda$: Here the two solutions $\phi_\pm$ are real only if

$$T < T_+ = \frac{T_0}{\sqrt{1 - \frac{\alpha^2}{4\gamma\lambda}}} \,.$$

On can easily verify that for $T > T_0$ the solutions $\phi_\pm$, if real-valued, are both positive. Knowing that $\phi_0 = 0$ is a local minimum, we can conclude that ϕ_+ is the other local minimum. A discontinuous phase transition is expected when both minima are equally deep, i.e. $F(\phi_0) = F(\phi_+)$, leading to

$$T_c = \frac{T_0}{\sqrt{1 - \frac{2\alpha^2}{9\gamma\lambda}}}$$

(d) Simply evaluate the difference at $T = T_c$:

$$\Delta\phi = \phi_+ - \underbrace{\phi_0}_{=0}\Big|_{T=T_c} = \frac{2T_0\alpha\sqrt{\gamma}}{\sqrt{\lambda}\sqrt{9\gamma\lambda - 2\alpha^2}}$$

(Σ = 12P)